Claims

1.    A    method    of    production    of    an
5   organoalkoxydialkylsilane of formula:
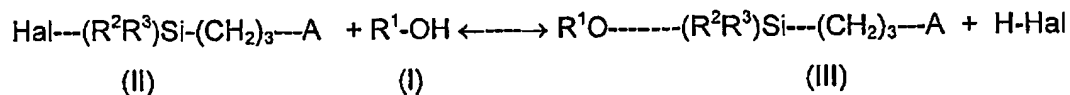
$$R^1O\text{------}(R^2R^3)Si\text{---}(CH_2)_3\text{---}A \qquad \text{(III)}$$

+ which comprises bringing an alcohol of formula:

$$R^1\text{-OH} \qquad \text{(I)}$$

10   into contact with a silane of formula:

$$Hal\text{---}(R^2R^3)Si\text{-}(CH_2)_3\text{---}A \qquad \text{(II)}$$
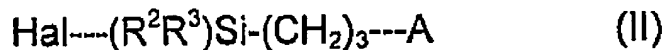
in order to carry out the reaction of alcoholysis of said
silane according to the following equilibrium reaction:

$$Hal\text{---}(R^2R^3)Si\text{-}(CH_2)_3\text{---}A \ + R^1\text{-OH} \longleftrightarrow R^1O\text{-------}(R^2R^3)Si\text{---}(CH_2)_3\text{---}A \ + \ H\text{-Hal}$$
$$\text{(II)} \qquad\qquad\qquad \text{(I)} \qquad\qquad\qquad\qquad \text{(III)}$$

15   where:
   -   the symbol Hal represents a halogen atom selected from
       the chlorine, bromine and iodine atoms,
   -   the symbols $R^1$, which may be identical or different,
       each represent a monovalent hydrocarbon group selected
20     from a linear or branched alkyl radical having from 1
       to   15   carbon   atoms   and   a   linear   or   branched
       alkoxyalkyl radical having from 2 to 8 carbon atoms;
   -   the symbols $R^2$ and $R^3$, which may be identical or
       different,   each   represent   a   monovalent   hydrocarbon
25     group selected from a linear or branched alkyl radical
       having from 1 to 6 carbon atoms and a phenyl radical;

- A represents a detachable group selected from: either a halogen atom Hal among the chlorine, bromine and iodine atoms; or a para-$R^0$-$C_6H_4$-$SO_2$-O- radical where $R^0$ is a linear or branched $C_1$-$C_4$ alkyl radical; or an $R^0$-$SO_2$-O- radical where $R^0$ is as defined above; or an $R^0$-CO-O- radical where $R^0$ is as defined above;

+ by working, under a pressure equal to or different from atmospheric pressure, in a stirred reactor equipped with a distillation column and with a condenser with possibility of reflux;

+ by carrying out, on the one hand, the said bringing into contact by pouring the alcohol of formula (I) into a mixture of silane of formula (II) + organic solvent(s) phase, it being possible for the solvent(s) phase to be used - partly - if necessary, mixed with the alcohol of formula (I), and on the other hand the removal of the halogenated acid formed of formula H-Hal by entrainment by means of said organic solvent(s) phase, and

+ by recovering the organoalkoxydialkylsilane of formula (III) formed in the reactor by any suitable method known by a person skilled in the art;

said process being characterized by the following points:

• the mixture of silane of formula (II) + organic solvent(s) phase is heated to a temperature that corresponds to its boiling point in the pressure conditions prevailing during execution of the process, and introduction of the alcohol begins when the condenser on the reactor is charged and is operating in conditions of steady-state reflux;

• the solvent(s) phase comprises one or more organic solvents selected so as to be able to fulfill a dual function: on the one hand, remove the halogenated acid formed by entrainment and salting-out of the gas owing to very low affinity of said phase for the acid, and on the other hand to provide liquid-vapour equilibrium with the alcohol which provides a concentration of

alcohol of formula (I) in the mixture of alcohol of formula (I) + organic solvent(s) phase in the range from 5 to 30 wt.%;

- the manner of introduction of the alcohol of formula (I) follows an operating procedure that is designed to prevent, at any moment during the reaction of alcoholysis of the silane of formula (II), accumulation of the halogenated acid of formula H-Hal in the reactor by dissolution in the alcohol of formula (I), in such a way that the amount of halogenated acid entrained by the solvent(s) phase represents, at any moment during the reaction of alcoholysis of the silane of formula (II), more than 90 wt.% of the halogenated acid formed;

- the total amount of alcohol of formula (I) introduced is such that the molar ratio of alcohol of formula (I) to silane of formula (II) is in the range from 1 to a value below 3;

- the amount of solvent(s) phase present in the reactor along with the silane of formula (II) depends on the nature of this phase and is determined so as to make it possible to limit, during introduction, the concentration of alcohol of formula (I) in the mixture of alcohol of formula (I) + organic solvent(s) phase in the aforesaid range from 5 to 30 wt.%.

2.      The method as claimed in claim 1, characterized in that the solvent(s) phase comprises solvent(s) whose boiling point, in the conditions of pressure prevailing during execution of the method, is close to that of the alcohol of formula (I).

3.      The method as claimed in claim 1 or 2, characterized in that the manner of introduction of the alcohol of formula (I) is based on operating procedure VA1, comprising:

- at least two charges of two fractions of alcohol, the first fraction of alcohol corresponding to a proportion representing 60 to 90 mol.% relative to the total molar quantity of alcohol used,
- at least two periods of reflux without charging, each of them subsequent to each alcohol charge effected;
- the flow rate and the charging time of each fraction of alcohol as well as the duration of each period of reflux without charging being controlled in such a way that each fraction of alcohol charged is consumed during the period of reflux without charging that follows said charging.

4.    The method as claimed in claim 1 or 2, characterized in that the manner of introduction of the alcohol of formula (I) is based on operating procedure VA2, which comprises execution of a single continuous charge of alcohol, but employing a flow rate that decreases with the degree of progress of the reaction of alcoholysis of the silane of formula (II) in such a way that the rate of introduction of the alcohol tracks its rate of consumption, and this single charging stage can be extended by a period of reflux without charging of variable duration.

5.    The method as claimed in any one of the claims 1 to 4, characterized in that it employs an anhydrous alcohol containing less than 1000 ppm of water and the total quantity of alcohol of formula (I) introduced is such that the molar ratio of alcohol of formula (I) / silane of formula (II) is in the range from 1.05 to 2.5.

6.     The method as claimed in any one of the claims 1 to 5, characterized in that it employs a quantity of solvent(s) phase that is determined so as to provide a concentration of alcohol of formula (I) in the combination of alcohol of formula (I) + solvent(s) phase that is in the range from 10 to 30 wt.%.

7.     The method as claimed in any one of the claims 1 to 6, characterized in that the method is carried out with reactants of formulas (I) and (II) where:
- the symbol Hal represents a halogen atom selected from the atoms of chlorine, bromine and iodine;
- the symbols $R^1$ are selected from the methyl, ethyl, n-propyl, isopropyl, n-butyl, $CH_3OCH_2-$, $CH_3OCH_2CH_2-$ and $CH_3OCH(CH_3)CH_2-$ radicals;
- the symbols $R^2$ and $R^3$ are selected from the radicals: methyl, ethyl, n-propyl, isopropyl, n-butyl, n-hexyl and phenyl.
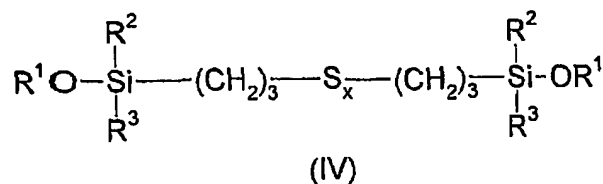
8.     The method as claimed in claims 1, 2 and 7, characterized in that, when the method is carried out using an alkanol of formula (I) where $R^1$ is selected from the methyl, ethyl, n-propyl and isopropyl radicals, the solvent or solvents that is/are very suitable is/are selected from hexane, heptane, and cyclohexane used alone or mixed with one another and/or mixed with pentane.

9.     The method as claimed in any one of the claims 1 to 8, characterized in that, at the end of the alcoholysis reaction, distillation of the reaction mixture is carried out in order to remove the unconsumed alcohol and the solvent(s) phase which can easily be recycled to a new reaction of alcoholysis.

10.    The method as claimed in claim 9, characterized in that, in the case of recycling, the following sequence of operations is carried out:

- introduction of the distillate based on alcohol and
5  solvent(s) obtained from a previous operation, into the reactor containing a new charge of silane of formula (II), if necessary adding fresh alcohol and/or additional solvent(s) phase so that the concentration of alcohol of formula (I) in the mixture of alcohol of formula (I) +
10  organic solvent(s) phase is within the range from 5 to 30 wt.%;

- then heating the mixture to raise its temperature to the value corresponding to its boiling point in the conditions of pressure prevailing during execution of the
15  method and establishment of conditions with total steady-state reflux;

- then carrying out a period of reflux without charging of alcohol during the time required for chemical consumption of the alcohol present in the reaction
20  mixture;

- then charging, either in batch mode or continuously, of the extra amount of alcohol required so that the molar ratio of total alcohol of formula (I) to silane of formula (II) is in the range from 1 to a value of less
25  than 3;

- then completion of the reaction by carrying out a second period of reflux without charging to reach a degree of transformation (TT) of the silane of formula (II) equal to at least 96 mol.%.

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11.    A method of production of the polysulfides of average general formula (IV):
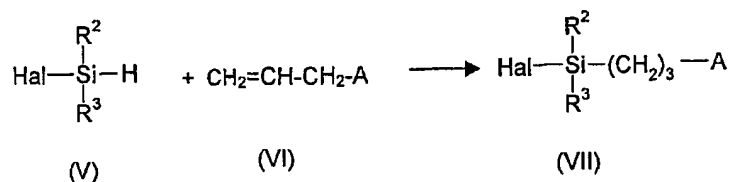
$$R^1O-\underset{\underset{R^3}{|}}{\overset{\overset{R^2}{|}}{Si}}-(CH_2)_3-S_x-(CH_2)_3-\underset{\underset{R^3}{|}}{\overset{\overset{R^2}{|}}{Si}}-OR^1$$

(IV)

in which:

- x is an integer or a fractional number, in the range from 1.5 ± 0.1 to 5 ± 0.1; and

5    - the symbols $R^1$, $R^2$ and $R^3$ are as defined above, characterized in that it is carried out as a sequence of stages (a), (b) and (c), in the definition of which the detachable group A corresponds to the symbol Hal representing a halogen atom and is a chlorine atom:

10   + stage (a) corresponding to the process taking place according to the equation:

$$Hal-\underset{\underset{R^3}{|}}{\overset{\overset{R^2}{|}}{Si}}-H \quad + \quad CH_2=CH-CH_2-A \quad \longrightarrow \quad Hal-\underset{\underset{R^3}{|}}{\overset{\overset{R^2}{|}}{Si}}-(CH_2)_3-A$$

(V)              (VI)                    (VII)

where:

- the symbol Hal represents a chlorine atom, and

15   - the symbols A, $R^2$ and $R^3$ are as defined above,

the reaction being carried out:

- by reacting, at a temperature in the range from -10°C to 200°C, one mole of the diorganohalosilane of formula (V) with a stoichiometric or non-stoichiometric molar

20   quantity of the allyl derivative of formula (VI), working, in a homogeneous or heterogeneous medium, in the presence of an initiator comprising:

- either a catalytic activator comprising: (i) at least one catalyst containing at least one transition metal

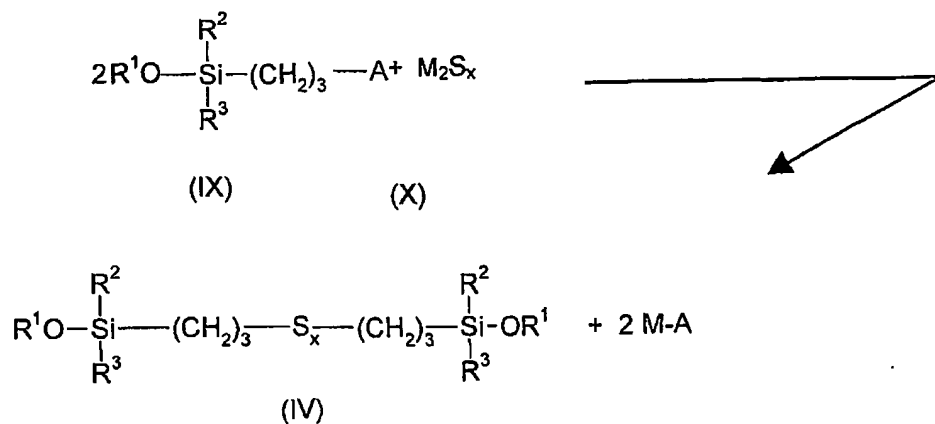25   or a derivative of said metal, taken from the group

comprising Co, Ru, Rh, Pd, Ir and Pt; and optionally
(2i) at least one hydrosilylation reaction promoter or
auxiliary,
- or a photochemical activator, in particular comprising
5    suitable ultraviolet radiation or suitable ionizing
radiation,
and optionally isolating the diorganohalosilylpropyl
derivative of formula (VII) formed;
+ stage (b) corresponding to the process described in any
10   one of the preceding claims 1 to 10;
+ and stage (c) corresponding to the process employing
the reaction:

$$2R^1O-\underset{\underset{R^3}{|}}{\overset{\overset{R^2}{|}}{Si}}-(CH_2)_3-A^+ \; M_2S_x$$

(IX)                    (X)

$$R^1O-\underset{\underset{R^3}{|}}{\overset{\overset{R^2}{|}}{Si}}-(CH_2)_3-S_x-(CH_2)_3-\underset{\underset{R^3}{|}}{\overset{\overset{R^2}{|}}{Si}}-OR^1 \;\; + \; 2\,M\text{-}A$$

(IV)

where:
15  - the symbols $R^1$, $R^2$, $R^3$, A and x are as defined above,
and
- the symbol M represents an alkali metal,
the reaction being carried out:
- by reacting, at a temperature in the range from 20°C to
20   120°C, either the reaction mixture obtained at the end of
stage (b), or the monoorganooxydiorganosilylpropyl
derivative of formula (IX) used separately after
separation from said reaction mixture, with the metal
polysulfide of formula (X) in the anhydrous state, using
25   0.5 ± 15 mol.% of metal polysulfide of formula (X) per
mole of reactant of formula (IX) and optionally working

in the presence of an inert polar (or nonpolar) organic solvent, and

- isolating the bis-(monoorganooxysilylpropyl) polysulfide of formula (I) formed.

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12. The method as claimed in claim 11, characterized in that stage (a) is carried out in the presence of an activator comprising, as the catalyst or catalysts (i), one and/or another of the following metallic species: (i-1) at least one finely-divided elemental transition metal; and/or (i-2) a colloid of at least one transition metal; and/or (i-3) an oxide of at least one transition metal; and/or (i-4) a salt derived from at least one transition metal and an inorganic carboxylic acid; and/or (i-5) a complex of at least one transition metal provided with organic ligand(s) that can possess one or more heteroatom(s) and/or with organosilicon ligand(s); and/or (i-6) a salt as defined above where the metallic part is provided with ligand(s) as also defined above; and/or (i-7) a metallic species selected from the aforementioned species (elemental transition metal, oxide, salt, complex, complexed salt) where the transition metal is associated in this case with at least one other metal selected from the family of the elements of groups 1b, 2b, 3a, 3b, 4a, 4b, 5a, 5b, 6b, 7b, and 8 (except Co, Ru, Rh, Pd, Ir and Pt) of the periodic table as published in the Handbook of Chemistry and Physics, 65th edition, 1984-1985, CRC Press, Inc., said other metal being used in its elemental form or in a molecular form, said association possibly giving rise to a bimetallic or multimetallic species; and/or (i-8) a metallic species selected from the aforementioned species (elemental transition metal and association of transition metal – other metal; oxide, salt, complex and complexed salt based on a transition metal or based on an association of transition metal – other metal) which is supported on an

inert solid support such as alumina, silica, carbon black, a clay, titanium dioxide, an aluminosilicate, a mixture of oxides of aluminum and zirconium, a polymeric resin.

13. The method as claimed in claim 11 or 12, characterized in that stage (a) is carried out in the presence of an activator comprising:

+ as the catalyst or catalysts (i), at least one metallic species belonging to the iridium complexes of formula:

$$[Ir \, (R^4)_y \, (R^5)]_z \qquad (XI)$$
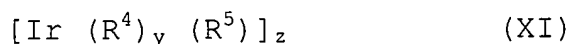
in which:

- the symbol $R^4$ represents either a monodentate ligand L and in this case $y = 2$, or a bidentate ligand $(L)_2$ and in this case $y = 1$, and

- the symbol $R^5$ represents either Hal as defined above, and in this case $z = 2$, or a ligand of type LX and in this case $z = 1$;

+ and as the possible auxiliary or auxiliaries (2i), at least one species in the free state or supported, selected from the group of compounds comprising:

    (i)    the ketones,

    (ii)   the ethers,

    (iii)  the quinones,

    (iv)  the anhydrides,

    (v)   the unsaturated hydrocarbons (UHC) having an aromatic character and/or containing at least one C=C double bond and/or at least one C≡C triple bond, where these unsaturated bonds can be conjugated or unconjugated, said UHCs being linear or cyclic (mono- or polycyclic), having from 4 to 30 carbon atoms, having from 1 to 8 ethylenic and/or acetylenic unsaturations and optionally containing one or more heteroatoms,

(vi)   and mixtures thereof,

with the condition that when the auxiliary comprises one or more UHC as defined above, this UHC or these UHCs is/are mixed with at least one other auxiliary different
5   from a UHC.

14.   The method as claimed in any one of the claims 11 to 13, characterized in that stage (c) is carried out using anhydrous metal polysulfides of formula (X) which are prepared beforehand from an alkali metal sulfide $M_2S$
10   in the form of a hydrated sulfide, by a process involving a sequence of the following steps (1) and (2):

- step (1), involving dehydration of the hydrated alkali metal sulfide by applying a suitable method by which the water of crystallization can be removed while
15   keeping the alkali metal sulfide in the solid state, throughout the dehydration step;

- step (2), in which one mole of dehydrated alkali metal sulfide obtained is then brought into contact with $n(x-1)$ moles of elemental sulfur, working at a temperature
20   in the range from 20°C to 120°C, optionally under pressure and also optionally in the presence of an anhydrous organic solvent, the aforementioned factor n being in the range from 0.8 to 1.2 and the symbol x being as defined above.